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## Chemical Process for Making Dialdehyde Starch

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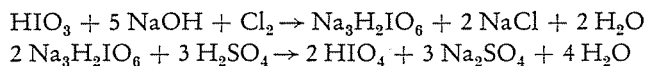
*A practical, strictly chemical process has been developed for the periodic acid oxidation of starch to dialdehyde starch. In the procedure spent oxidant is converted by alkaline hypochlorite to insoluble sodium paraperiodate, which is recovered in high yield for recycling. The process is suitable for small-scale production of dialdehyde starches of various carbonyl contents.*

*(Zusammenfassung siehe Seite 44; Résumé à la page 44)*

### Introduction

Dialdehyde starch (DAS) is manufactured on a large scale in the United States [1] and in Japan [2] by the periodic acid oxidation of corn starch. In these processes electrolytic regeneration of the spent oxidant [3, 4] is utilized and a large capital outlay for specialized equipment is required [3]. Occasionally for various commercial applications, small

amounts of periodic acid-oxidized polysaccharides having a wide range of carbonyl contents are required [5, 6]. In such cases the expense of costly electrolytic equipment is not warranted, and it would be desirable to have a strictly chemical process for converting the iodic acid in spent liquors to periodic acid for reuse. Simple procedures are known for preparing periodic acid in high yield from iodic acid [7] as shown in the equations below.



Optimum conditions for the periodic acid oxidation of starch to DAS [3, 8] have also been previously established. Detailed data are lacking, however, on product and spent oxidant recovery for these reactions.

This paper describes an efficient, practical method to make DAS having a carbonyl content of at least 97 % of theory. The process is based upon a materials balance study of five consecutive small-scale oxidations of starch utilizing periodic acid regenerated chemically from successive spent liquors. Carbonyl contents of DAS of a fraction of a percent and up may be prepared by using the equivalent amount of periodic acid in the oxidation. The simplicity of the process should permit scale-up with little difficulty.

## Experimental

### Periodic Acid

To determine the unreacted periodic acid and the iodic acid in spent oxidation liquors and the purity of crude sodium paraperiodate, the method of *Fleury* and *Lange* [9] was modified. To a solution containing about 0.03 g of periodic acid neutralized with alkali in a 125-ml Erlenmeyer flask, is added 10 ml of a saturated solution of sodium bicarbonate and then immediately 5 ml of 0.1 N sodium arsenite solution and 1 ml of a 20 % basic potassium iodide solution. The mixture is allowed to stand for 15 min. Excess arsenite is titrated with 0.1 N iodine solution using starch indicator.

$$\text{g HIO}_4 = (5 \text{ ml arsenite} \times \text{normality} - \text{ml I}_2 \times \text{normality}) \times 0.09597.$$

### Iodic Acid

To a solution containing about 0.03 g of iodic acid neutralized with alkali and diluted to 15 ml with water in a 125-ml Erlenmeyer flask is added 1 ml of ethylene glycol. The solution is acidified to pH 3.5–5 and allowed to stand at least 15 min to reduce any periodate present to iodate. Next 3 ml of 0.5 N sulfuric acid and 2 ml of basic potassium iodide solution are added and after standing for 2 min the iodine liberated is titrated with 0.1 N sodium thiosulfate solution using starch indicator.

$$\text{g HIO}_3 = \text{ml Na}_2\text{S}_2\text{O}_3 \times \text{normality} \times 0.02932$$

### Carbonyl Content of Dialdehyde Starch

Analyses for carbonyl content of DAS were performed by a modification of the spectrophotometric method of *Wise* and *Mehlretter* [10]. The *p*-nitrophenylhydrazone precipitate obtained in the original procedure is dissolved in warm ethylene glycol monomethyl ether instead of hot 95 % ethanol. The solution is transferred to a 200-ml volumetric flask and adjusted to volume with the new solvent before absorbance is measured.

### Preparation of Sodium Paraperiodate

Iodine (100 g) was oxidized to sodium iodate with 125 g of sodium chlorate according to the procedure of *Willard* [7]. The reaction required about 3 h for completion at a temperature of 45–50 °C. The sodium iodate in solution was then converted to sodium paraperiodate as follows: To the stirred sodium iodate solution in a 2-liter beaker was added 200 ml of water followed by 140 g of sodium hydroxide pellets. The hot solution was then maintained at 90–95 °C in a steam bath and 75 g of chlorine passed into the mixture during 1 h. The reaction mixture was then adjusted to pH 11.5 by addition of 50 wt percent solution of sodium hydroxide to complete the conversion to insoluble sodium paraperiodate. After cooling the reaction mixture to room temperature the product was filtered by suction on a fritted glass funnel of medium porosity and washed once on the filter with cold water. The crude sodium paraperiodate was dried at 110 °C and weighed 223.4 g (theory, 231.6 g). Calculated weight of  $\text{Na}_3\text{H}_2\text{IO}_6$  (from periodate analysis) in 223.4 g of product was 225.1 g and indicated the presence of some  $\text{Na}_2\text{H}_3\text{IO}_6$ . Yield of recovered product was therefore 97 % of theory.

### Periodic Acid Oxidation of Starch to Dialdehyde Starch

A stirred slurry of 136.2 g of the sodium paraperiodate (equivalent to 89.6 g  $\text{HIO}_4$  by analysis) in 400 ml of water in a 1-liter beaker was treated with about 75 ml of 50 wt percent of sulfuric acid added in portions to obtain a pH of 1.5. The beaker was placed in a circulating water bath for temperature control and the solution cooled to about 20 °C before the reaction with starch. Unmodified corn starch, 77.0 g (68.8 g; dry basis) slurried in 100 ml of water, was added to the periodic acid solution and the temperature of the reaction was maintained at about 32 °C with the circulating water bath. The reaction mixture was stirred for 4 h at 32 °C  $\pm$  2 °C. The dialdehyde starch that was produced was then filtered by suction on a fritted glass funnel of medium porosity, washed five times by slurrying in 200 ml of water each time, and filtering. Removal of spent oxidant was followed by analysis of the individual washes. The colorless filtrate from the oxidized starch was also analyzed for iodic acid and unreacted periodic acid. Figure 1 illustrates the amount of iodic and unreacted periodic

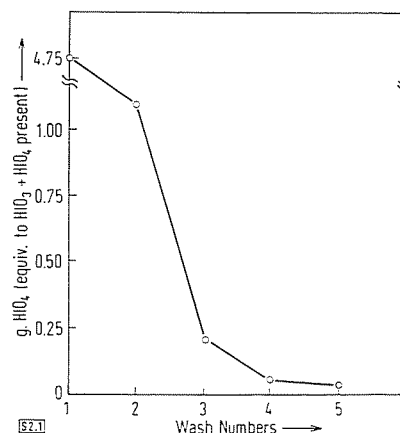


Figure 1.  $\text{HIO}_3$  and  $\text{HIO}_4$  in successive dialdehyde starch washes calculated as  $\text{HIO}_4$ .

Table 1. Dialdehyde Starch and Oxidant Recovery from Five Consecutive Reactions.

Dialdehyde starch			HIO <sub>4</sub> equivalent of			Na <sub>3</sub> H <sub>2</sub> IO <sub>6</sub> recovery %
g <sup>1)</sup>	Yield % of theory	Carbonyl % of theory	Na <sub>3</sub> H <sub>2</sub> IO <sub>6</sub> <sup>2)</sup> used g	Spent <sup>3)</sup> oxidant g	Recovered <sup>2)</sup> Na <sub>3</sub> H <sub>2</sub> IO <sub>6</sub> g	
67.4	99.1	97	89.6	89.3	88.4	98.6
67.1	98.7	97	89.6	90.6	87.0	97.0
67.2	98.8	98	89.6	89.5	88.0	98.2
67.4	99.1	98	89.6	89.9	87.0	97.0
67.4	99.1	98	89.6	89.6	87.7	97.9

1 Dry basis.

2 HIO<sub>4</sub> equivalent calculated from the periodate found by analysis of the crude Na<sub>3</sub>H<sub>2</sub>IO<sub>6</sub>.

3 HIO<sub>4</sub> equivalent to HIO<sub>3</sub> and unreacted HIO<sub>4</sub> found by analysis of the combined filtrate and washings of DAS.

acids removed from the product in each wash, calculated as periodic acid for comparison with the periodic acid equivalent of 89.6 g originally used.

The white dialdehyde starch was dried in a forced draft oven at 60 °C overnight and weighed 67.4 g (dry basis). Analysis for carbonyl content showed that the product was at least 97 % dialdehyde starch.

Five consecutive oxidations of starch were made in which periodic acid regenerated from the previous run was used; the yields and analyses of the dialdehyde starches are given in Table 1.

#### Conversion of Spent Oxidant to Sodium Paraperiodate

Washings from the dialdehyde starch product were combined (1,000 ml) and concentrated in a vacuum rotary evaporator to 200 ml and added to the original filtrate (900 ml) of the product. The spent oxidant solution after analysis for iodic acid and unreacted periodic acid present was placed in a 2-liter beaker and adjusted to pH 7 with 50 wt percent sodium hydroxide. Sodium hydroxide pellets (83.7 g) were then added gradually with stirring. The rest of the procedure used for the initial preparation of sodium paraperiodate was then followed; 45 g of chlorine was added during 40 min of reaction at 90–95 °C. The dried crude sodium paraperiodate weighed 135.9 g. It assayed to be equivalent to 88.4 g periodic acid.

Periodic acid recovery data for the five starch oxidations are recorded in Table 1. After the first oxidation, 3 % makeup of sodium paraperiodate was added because of the nearly 3 % loss of oxidant in the recovery step.

#### Discussion

Dialdehyde starch having a carbonyl content of at least 97 % of the theoretical was readily prepared in nearly quantitative yield by this chemical process. Recycling of the regenerated spent oxidant after addition of 3 % sodium paraperiodate makeup was successful for five starch oxidation reactions carried out consecutively. Spent oxidant was collected quantitatively and its oxidation by alkaline hypochlorite permitted 97 % or better recovery of the iodic and unreacted periodic acids present, as insoluble sodium paraperiodate. By this means also such impurities in corn starch as fatty acids and protein that may have leached into the

spent liquors were removed from the crude sodium paraperiodate during its isolation by filtration and therefore did not build up in the successive reactions. Conversion of the insoluble crude sodium paraperiodate to periodic acid in aqueous solution by addition of sulfuric acid also produced sodium sulfate in solution. The presence of this salt aided in the reduction of swelling of the starch granules during oxidation and thus allowed more rapid filtration of the DAS product. The chief advantage of the chemical process, however, is that it avoids the use of expensive electrolytic equipment for regeneration of spent oxidant for recycling in the process.

#### Zusammenfassung

**Chemisches Verfahren zur Herstellung von Dialdehydstärke.** Für die Perjodsäureoxydation von Stärke zu Dialdehydstärke wurde ein praktisches, streng chemisches Verfahren entwickelt. Bei diesem Prozeß wird das zugesetzte Oxydationsmittel durch alkalisches Hypochlorit in unlösliches Natrium-Paraperiodat umgewandelt, welches in hoher Ausbeute für die Rückführung wiedergewonnen wird. Das Verfahren ist für die Produktion von Dialdehydstärken mit verschiedenen Carbonylgehalten in kleinerem Maßstab geeignet.

#### Résumé

**Procédés chimiques pour la fabrication de l'amidon dialdéhyde.** Un procédé pratique, strictement chimique a été développé pour l'oxydation périodique de l'amidon en amidon dialdéhyde. Au cours de ce processus l'agent oxydant utilisé est converti par l'hypochlorite alcalin en parapériodate de sodium insoluble. Ce procédé est approprié pour une production d'amidon dialdéhyde à petite échelle d'une teneur en groupements carbonyl variable.

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